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(64) Thickened moulding compositions.

(57) A reinforced unsaturated resin composition contains an unsaturated polymer, e.g. an unsaturated polyester, a vinyl ester polymer or a urethane acrylate polymer, a vinyl monomer and, as thickener, a crystalline polyester.

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THICKENED MOULDING COMPOSITIONS

This invention relates to thickened reinforced unsaturated resin compositions suitable for moulding.

Moulding compositions based on unsaturated polyester resins normally consist of resin, filler, catalyst for curing, internal mould release agents and reinforcing fibres. The original compositions were in the form of a putty - known as "dough moulding compounds" (DMC). Following the discovery that the incorporation of certain Group II oxides and hydroxides such as CaO , $\text{Ca}(\text{OH})_2$, MgO , $\text{Mg}(\text{OH})_2$ caused thickening of the resin system, compositions known as "bulk moulding compounds" (BMC) which were tack free and "sheet moulding compounds" (SMC) became available. BMC was originally based on chopped glass fibres whilst SMC was based on chopped strand mat and, after compacting, was rolled up between sheets of polyethylene. After about 3 days the polyethylene could be readily peeled off to yield a tack free sheet which could be loaded into a heated press and moulded at temperatures of $120-150^\circ\text{C}$ under pressure.

The thickening of resin by Group II metal oxides/hydroxides is due to a combination of the formation of covalent bonds and co-ordination bonds. It is difficult to control. Ideally the impregnation mix should be low in viscosity to allow good impregnation of the fibres, should thicken rapidly after impregnation and should reach a maximum viscosity which does not change on storage. Such behaviour is represented by a graph of viscosity vs. time (days) marked "IDEAL" in the accompanying drawing. What actually happens when using such metal oxides/hydroxides is also shown in another graph of the accompanying drawing marked "TYPICAL SMC". The rate and extent of thickening

depends on the resin used to such an extent that not only the normal resin parameters have to be controlled (i.e. acid value and viscosity) but also hydroxyl value and molecular weight distribution. In addition, since the metal oxide/
5 hydroxide is influenced by the presence of moisture and carbon dioxide in the atmosphere, special storage precautions are required to prevent even further variations in maturation on storage.

It is also known to make other types of thermosetting
10 resins, e.g. vinyl esters, into BMCs and SMCs, but it has previously been necessary to make special modifications to the resins to allow the thickening reaction with Group II oxides and hydroxides to occur, this being because the standard vinyl ester resins often have very low acid values.

15 All of the abovementioned compositions were highly filled, but if unfilled systems were required either the filler was omitted or a solvent based resin was pre-impregnated on to reinforcing fibres, the solvent removed and the resulting tacky prepreg rolled up between sheets of film.
20 However, the sheets of film were difficult to remove from these prepregs due to the tackiness of the pre-impregnated fibre.

One method of overcoming the disadvantages with unfilled pre-impregnated reinforcements is described in B.P. 1,319,243
25 and B.P. 1,318,517. Examples are given in these patents of polyester resins which when blended with styrene monomer are solid and can be used to impregnate reinforcing fibres when molten.

We now find surprisingly that crystalline polyester
30 resins can be used to thicken both filled and unfilled unsaturated polymer moulding compositions based on standard resins thus eliminating the need for special resins made for moulding compositions. Because the thickening mechanism is a

physical one a number of other advantages occur:-

(i) no metal oxide/hydroxide is required and hence, in contrast to when a metal oxide/hydroxide is used, no special storage precautions are required to prevent further variations in maturing,

(ii) indeed, no maturation period is required the compositions being ready for moulding as soon as they have cooled,

(iii) storage stability is much improved.

10 An unsaturated resin composition in accordance with the invention is reinforced and contains an unsaturated polymer, a vinyl monomer and, as a thickener, a crystalline polyester.

The crystalline polyester is preferably present in the 15 composition in an amount of from 10-50%, more preferably 15-40%, by weight of the total weight of unsaturated polymer, vinyl monomer and crystalline polyester.

The polyesters used as thickeners in compositions of the invention are those capable of crystallising by virtue 20 of their having a symmetrical structure. They are preferably unsaturated since then, they may also take part in the cross-linking reaction with the vinyl monomer during curing. They may be made by the reaction of symmetrical glycols such as neopentyl glycol, 1,6-hexanediol and 1,4-cyclohexanedimethanol 25 with an acid which may be fumaric acid alone or which may additionally contain a minor percentage of a symmetrical aromatic saturated di-acid, e.g. terephthalic acid. For ease of handling they may be dissolved in a vinyl monomer, preferably a vinyl aromatic monomer, e.g. styrene, and 30 incorporated in the composition in this form.

The unsaturated polymers to which the thickeners are added may be unsaturated polyesters such as those made by

reacting one or more glycols with an unsaturated dicarboxylic acid or its anhydride or with a mixture of the unsaturated dicarboxylic acid or anhydride with a saturated dicarboxylic acid or its anhydride. The unsaturated polyesters may be dissolved in a vinyl type monomer and incorporated in the composition in this form. Optionally, minor amounts of alcohols, polyols, monobasic or polybasic acids may be incorporated in the reaction mixtures from which the unsaturated polyesters are made, which reaction mixtures may also include dicyclopentadiene to modify the polyesters.

Other unsaturated polymers which can be made into resin compositions in accordance with the invention using these techniques are vinyl ester polymers (which may be prepared by reaction of acrylic or methacrylic acid with epoxy resins) and urethane acrylate polymers, especially acrylate terminated polyurethanes.

The resin composition may additionally contain a filler, which can be selected from, for example, natural or precipitated calcium carbonates, clays, silica, talc, mica and alumina hydrate.

The composition is reinforced either by admixing a reinforcement, preferably reinforcing fibres, with the other components of the composition or by impregnating it into a fabric made from reinforcement fibres, so providing a prepreg. Whilst the reinforcing fibres will normally be glass fibres they may be substituted wholly or in part by carbon fibres, KEVLAR (RTM) or similar aramid fibres, natural fibres e.g. jute, or synthetic fibres.

Pigments may be incorporated in the composition if required.

The compositions may be cured using free radical catalysts such as organic peroxy compounds e.g. t-butyl

perbenzoate or perketals but unfilled compositions may be cured using light as described in our co-pending European Patent Publication No. 0025359A.

Typical mould release agents which may additionally be incorporated in these compositions are zinc stearate and ZELEC (RTM) UN.

Any of the thermoplastics normally incorporated into SMC or BMC to reduce shrinkage may be incorporated in the composition e.g. polyethylene, acrylic co-polymers, polystyrene, saturated polyesters and polycaprolactones.

Preferred compositions embodying the invention will now be described in more detail with reference to the following Examples (Examples 1, 3 and 6 are outside the invention and are given for comparison).

15 Example 1 (Comparative)

A composition was prepared by mixing together under high shear:-

20	Polyester resin (2:1 maleate:phthalate ester of propylene glycol, 65% solution in styrene)	100 parts by weight
	Calcium carbonate	140 parts by weight
	Zinc stearate	5 parts by weight
	Tertiary butyl perbenzoate	1 part by weight
	Magnesium oxide	2.5 parts by weight

25 This was made up into a sheet moulding compound with 1" chopped glass rovings (83 parts by weight), by rolling between two polythene carrier films. Maturation for 3 days at 20°C was required before the polythene films could be stripped off leaving a stiff, non tacky compound mouldable
30 in matched steel moulds under pressure at 150°C.

Example 2

A composition was prepared by mixing together under

high shear at 60°C:-

	Polyester resin as in Example 1	60 parts by weight	18 1/2
	Crystalline resin	40 parts by weight	42 1/4
	(Neopentyl glycol fumarate, 70% solution in styrene)		3.6
5	Calcium carbonate	140 parts by weight	42
	Zinc stearate	5 parts by weight	1.5
	Tertiary butyl perbenzoate	1 part by weight	0.3

This mixture was impregnated into 1" chopped glass
roving (83 parts by weight) by the method of Example 1.

10 The resulting sheet moulding compound was immediately chilled to 20°C, when it was found that the polythene carrier films could be cleanly stripped off, and the compound was immediately ready for moulding as in Example 1.

Example 3 (Comparative)

15 A mixture was prepared by high shear mixing of:-

	Polyester resin	100 parts by weight
	(Propylene glycol fumarate, modified with dicyclopentadiene, 70% solution in styrene)	
	3,3,5-trimethyl-1,1-bisperoxybutyl cyclohexane -	

20		1 part by weight
	Magnesium oxide	4 parts by weight

This mixture was impregnated by hand, between two
polythene carrier films, into:-

	Woven glass fibre cloth	300 parts
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25 and consolidated by rolling.

Rapid thickening of the resin caused difficulty in
impregnation, and even after several days maturation at 20°C
the resulting compound remained sticky and unpleasant to
handle.

30 Example 4

A mixture was prepared by combining together under
high shear at 60°C:-

Polyester resin (as Example 3) 50 parts by weight
 Crystalline resin 50 parts by weight
 (1,6-hexanediol fumarate, 70% solution in styrene)
 3,3,5-trimethyl-1,1-bisperoxybutyl cyclohexane -

5 1 part by weight

The mixture was then impregnated at 60°C by the method of Example 3 into

Woven glass fibre cloth 300 parts.

The resulting compound was cooled to 20°C, when the 10 polythene carrier films could be immediately stripped off, and the slightly tacky material was then moulded as in Example 1 into a high strength heat-resistant laminate.

Example 5

A mixture was prepared by combining together under 15 high shear at 60°C:-

Vinyl Ester Polymer Resin 75 parts by weight
 (Reaction product of acrylic acid with an epoxy resin, 55% solution in styrene)
 Crystalline Resin (as Example 4) 25 parts by weight
 20 t-Butyl Perbenzoate 1 part by weight
 Alumina Hydrate (filler) 160 parts by weight
 Zinc Stearate (mould release agent) 5 parts by weight

The mixture (75 parts by weight) was then used to impregnate at 50°C 25 parts of 25mm length chopped glass 25 fibre between polyethylene carrier films to produce a sheet moulding compound which was rapidly cooled to 20°C. A firm, non-tacky material was obtained from which the polyethylene carrier film could be easily stripped before moulding. The material was moulded at 150°C and 1000 p.s.i. pressure for 30 3 minutes to produce moulded articles of excellent quality.

Example 6 (Comparative)

Using the same technique as in Example 5 without the

warming and cooling the following impregnation mix was used:-

	Vinyl Ester Resin (as Example 5)	100 parts by weight
	t-Butyl Perbenzoate	1 part by weight
	Alumina Hydrate	130 parts by weight
5	Zinc Stearate	5 parts by weight
	Magnesium Oxide (thickening agent)	3 parts by weight

When impregnated into chopped glass fibres to give a glass content of 25% the material remained wet, sticky and difficult to handle and mould even after several days 10 maturation.

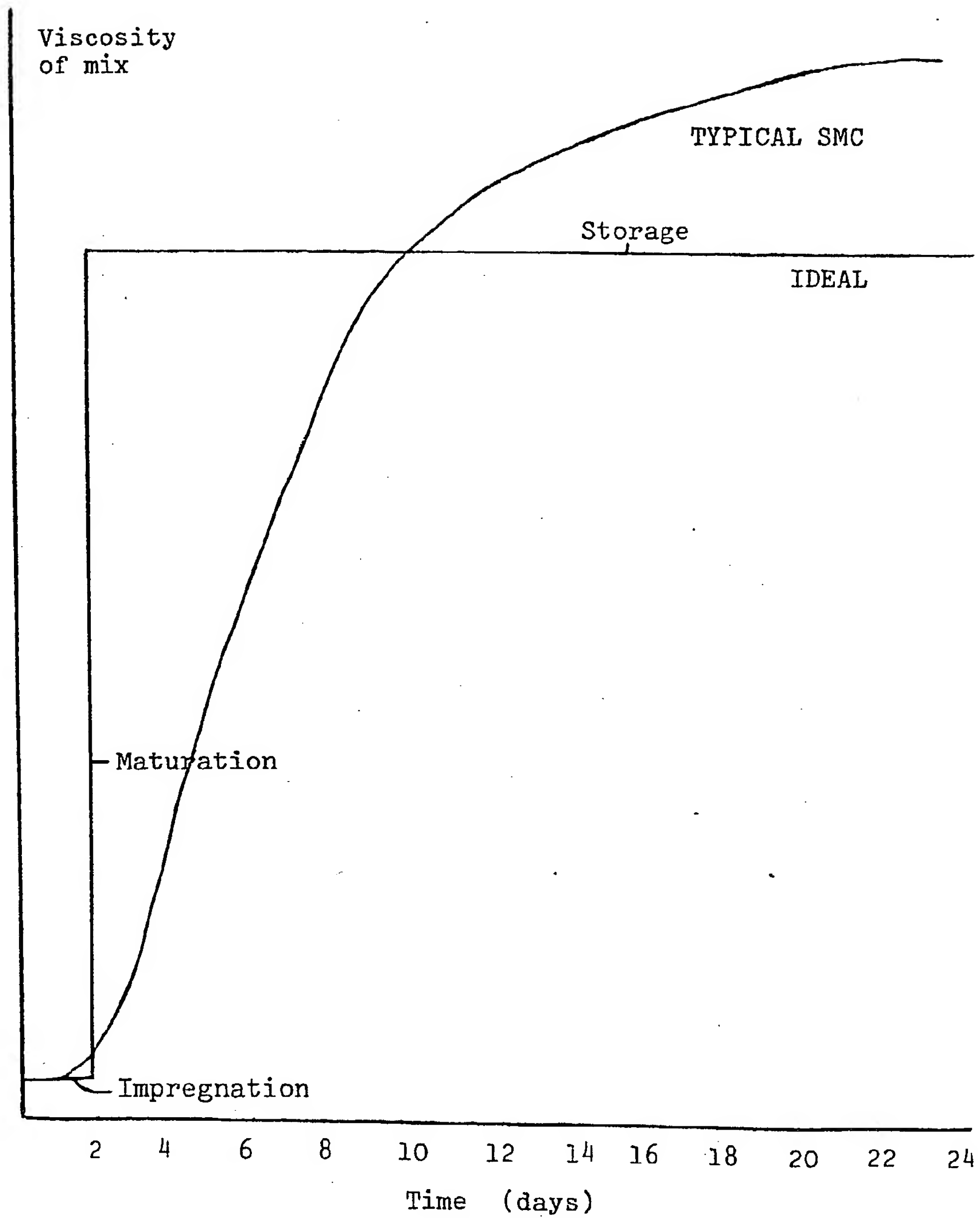
CLAIMS:

1. A reinforced unsaturated resin composition containing an unsaturated polymer, a vinyl monomer and a thickener, characterized in that the thickener is a crystalline polyester.
- 5 2. A reinforced resin composition according to claim 1, wherein the glycol of the crystalline polyester is neopentyl glycol, 1,6-hexanediol or 1,4-cyclohexanedimethanol.
3. A reinforced unsaturated resin composition according to claim 1 or claim 2, wherein at least a part of the acid of
10 the crystalline polyester is fumaric acid.
4. A reinforced unsaturated resin composition according to any one of the preceding claims, wherein at least a part of the acid is a symmetrical aromatic saturated dicarboxylic acid.
- 15 5. A reinforced unsaturated resin composition according to any one of the preceding claims, wherein the amount of crystalline polyester present in the composition is from 10 to 50% by weight of the total weight of the composition.
6. A reinforced unsaturated resin composition according to
20 any one of the preceding claims, wherein the unsaturated polymer is a polyester, a vinyl ester polymer or a urethane acrylate.
7. A reinforced unsaturated resin composition according to any one of the preceding claims which additionally contains a
25 filler.
8. A reinforced unsaturated resin composition according to any one of the preceding claims, which is a dough, bulk, or sheet moulding composition.

9. A reinforced plastics article formed by moulding a reinforced unsaturated resin composition characterized in that the resin composition is a composition according to any one of the preceding claims.

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EUROPEAN SEARCH REPORT

0083837

Application number

EP 82 30 6175

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
X	--- DE-A-2 725 133 (NIPPON GAKKI SEIZO K.K.) * Page 6, lines 1-8 ; page 11, lines 15-21 ; page 14, line 5 - page 15, line 9 ; claims 1-3, 6 ; examples 1-4 *	1-3, 5, 7-9	C 08 L 67/06 C 08 L 75/04 C 08 L 63/10 C 08 F 283/00 C 08 J 5/08
X	--- GB-A-1 007 168 (CIE DE SAINT-GOBAIN) * Page 1, line 49 - page 2, line 99 ; claims 1-4, 10, 11 *	1-3, 5, 7-9	
A	--- DE-A-2 447 852 (BASF AG) * Claims 1-3 ; page 6, line 30 - page 7, line 7 *	1-5, 7-9	
A	--- DE-A-2 402 739 (THE DOW CHEMICAL CO.) * Page 6, line 1 - page 9, line 11 *	1, 6-9	TECHNICAL FIELDS SEARCHED (Int. Cl. 3)
P, A	--- EP-A-0 052 958 (OLIN CORP.) * Claims 1, 2, 5 ; page 1, line 1 - page 2, line 36 *	1, 6-9	C 08 F 283/00 C 08 L 63/10 C 08 L 67/06 C 08 L 75/00 C 08 J 5/08
The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 18-02-1983	Examiner IDEZ C.G.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	